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HIGH-THROUGHPUT FABRICATION OF NANOCONE SUBSTRATES THROUGH POLYMER INJECTION MOULDING FOR SERS ANALYSIS IN MICROFLUIDIC SYSTEMS

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ABSTRACT

Metal-coated nanostructured surfaces have shown promise as substrates for surface-enhanced Raman spectroscopy (SERS) as they allow chemical trace detection with high sensitivity and rapid response. This sensitivity and specificity makes SERS especially interesting for environmental and biological analysis. Metal-capped silicon nanopillars, fabricated through a maskless ion etch, are state-of-the-art for on-chip SERS substrates. A dense cluster of high aspect ratio polymer nanocones was achieved by using high-throughput polymer injection moulding over a large area replicating a silicon nanopillar structure. Gold-capped polymer nanocones display similar SERS sensitivity as silicon nanopillars, while being easily integrable into a microfluidic chips.

KEYWORDS: Lithography-free, Reactive Ion Etching, Polymer Injection, Nanopillars, SERS, Sensors

INTRODUCTION

SERS utilizes noble metal nanostructures to amplify the Raman signal of small molecules through electromagnetic field enhancement by several orders of magnitude [1]. Maskless reactive ion etching (RIE) of silicon (Si) wafers produces uniform areas of free-standing nanopillars, which, after gold evaporation, result in isolated gold caps suitable for SERS detection [2]. This technique creates highly sensitive and reproducible plasmonic substrates in a scalable and cost-effective fashion. Our group has developed silicon nanopillar surfaces and applied them in the development of quantitative SERS sensors for biomedical sensing of hydrogen cyanide [3] and p-coumaric acid [4]. Subsequent integration of Si nanopillar chips into a centrifugal microfluidic platform for rapid and automated analysis of bacterial metabolites has been explored as well [5].

Microfluidic devices utilizing SERS often require an additional fabrication step or complex system integration strategies to allow SERS detection. Simplified integration of SERS sensing into microfluidic systems for multi-purpose Lab-on-a-Chip (LoC) applications is therefore highly sought after [6]. Injection moulding allows high-throughput fabrication of nanostructures for applications in the fields of superhydrophobic surfaces [7], as well as micro- and nanofluidic devices for biological sample handling [8]. Our work introduces the concept of utilizing high-throughput polymer injection moulding for the low-cost fabrication of gold-capped polymer nanocones for SERS sensing replicated from nano-patterned silicon based shims.

EXPERIMENTAL

Figure 1 illustrates the fabrication of polymer nanocones. We have developed a shim fabrication method that is based on maskless Si dry etching of microstructures to obtain Si nanocones (Fig. 1a). Polymer structures were then fabricated via injection moulding (Fig. 1c) from nickel shims (Fig. 1b) obtained from the Si templates. Subsequent gold evaporation resulted in the formation of metal nanocaps on the injection moulded nanocone tips, as illustrated in Figure 1d. The SERS capability of polymer nanocones compared to Si nanopillars was assessed utilizing Trans-l,2-bis(4-pyridyl)ethylene (BPE) as the benchmark analyte.

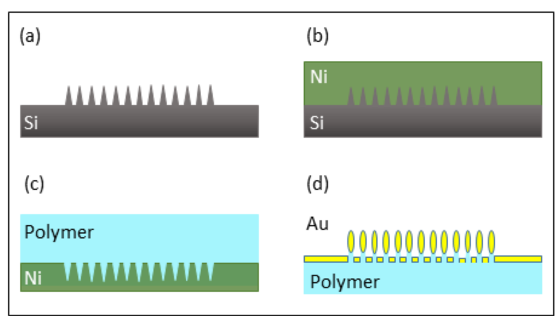

Figure 1: Fabrication procedure for polymer SERS substrates from Si nanocones through polymer-injection moulding of inverted structures with subsequent metal nanocap formation.

RESULTS AND DISCUSSION

Figure 2 shows gold-capped nanopillar structures on flat silicon substrates (Fig. 2a) as well as polymer injection moulded nanocones on flat polymer (Fig. 2b). Both substrates present morphological similarity over large areas. The SERS functionality of polymer nanocones, illustrated by depositing droplets of 100µM BPE as analyte in Fig. 2c, show comparable enhancement to Si nanopillars at relatively high analyte concentrations. The achieved polymer structures are compatible and can be easily integrated into microfluidic chips, as illustrated in Fig. 2d.

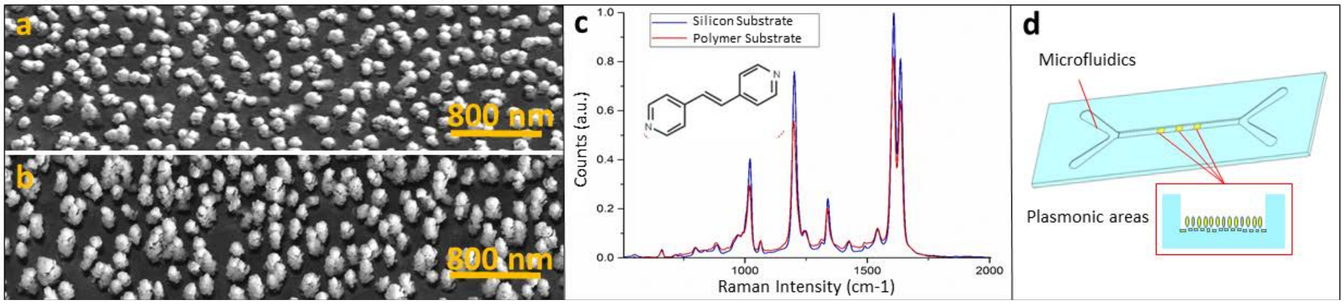

Figure 2: Gold-capped silicon nanopillars (a) and polymer nanocones (b) show comparable morphology. BPE signal of silicon nanopillars and polymer nanocones in comparison (c) illustrate comparable SERS functionalities. Polymeric nanocones can be utilized in injection-moulded microfluidics for SERS analysis (d).

CONCLUSION

We successfully fabricated gold-capped polymer nanocones from Si nanopillars utilizing high-throughput polymer injection moulding. Polymer nanocones display high density morphologies with a high aspect ratio. The structures can be utilized for SERS sensing of trace molecules with a similar sensitivity than Si nanopillars at high analyte concentrations. Integration in a LoC systems in a straight-forward manner is possible due to the polymeric nature of the substrate.

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